

Selective Mercury(II) Detection in Aqueous Solutions Upon the Absorption Changes Corresponding to the Transition Moments Polarized Along the Short Axis of an Azobenzene Chemosensor

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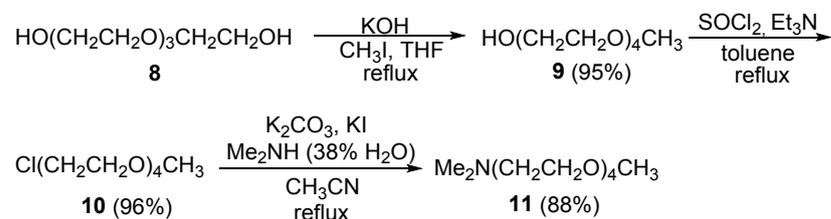
1. General remarks

¹H-NMR and ¹³C-NMR spectra were recorded with CDCl₃ as a solvent. Chemical shifts were determined relative to the residual solvent peaks (CHCl₃, $\delta = 7.26$ ppm for ¹H NMR, $\delta = 77.0$ ppm for ¹³C-NMR). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Mass spectra were recorded on a Thermo Scientific LTQ Orbitrap XL. All starting materials, reagents and organic solvents were purchased and used without further purification.

The used metal ion solutions were prepared by dissolving CuCl₂, NiCl₂·6H₂O, ZnCl₂, HgCl₂, CrCl₃·6H₂O, Mn(CH₃COO)₂, MgCl₂·6H₂O, CoCl₂·6H₂O, CaCl₂·2H₂O, FeCl₃, FeCl₂, KCl in buffered solutions. Studies were carried out in buffered conditions. The buffered conditions refer to the solutions contain 135 mM NaCl and 20 mM HEPES Buffer, at pH 7.4. The aqueous solutions of **1** and **7** were prepared in 50 μ M. All the solutions of metal ions are colorless, while the solutions of **1** with or without metal ions are very light yellow, by naked eyes. The UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 UV-Vis spectrophotometer, and all the related studies were carried out on fast scan mode with slit widths of 1.0 nm, using matched quartz cells. Test solutions were 200 μ L. All absorption scans were saved as ACS II files and further

processed in OriginLab software to produce all graphs shown. The wavelengths of UV and Vis photoirradiations are 365 nm and 520 nm, respectively.

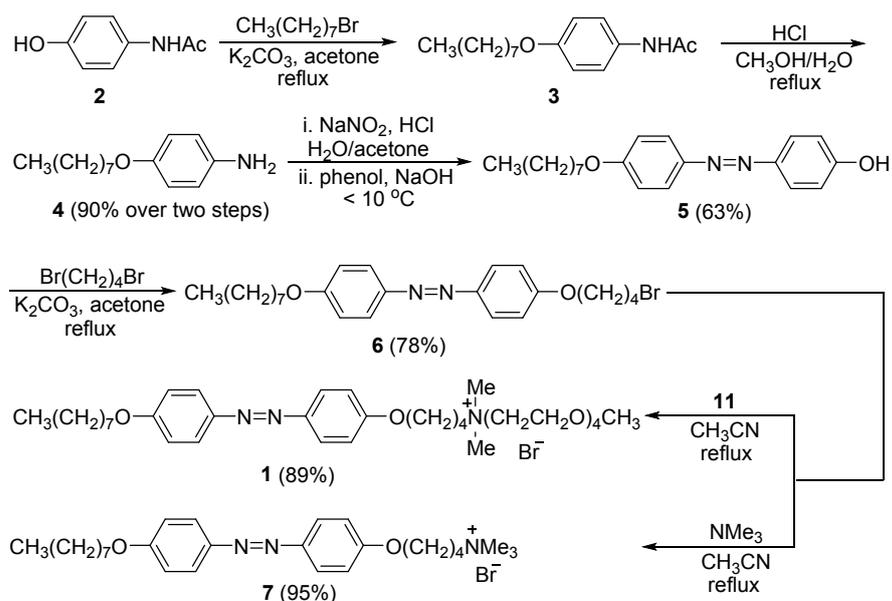
2. Experimental Section



2,5,8,11-tetraoxatridecan-13-ol (9): to a solution of **8** (5.00 mL, 28.96 mmol) in THF (30 mL) were added KOH (812 mg, 14.45 mmol, 1.0 eq) and CH₃I (0.90 mL, 14.45 mmol, 1.0 eq) slowly. The resulting mixture was refluxed overnight. The mixture was concentrated in vacuo and subsequently dissolved in EtOAc. The mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/CH₃OH = 20 : 1) to afford **9** (5.73 g, 95% yield) as colorless oil. ¹H NMR (500 MHz, CDCl₃)¹ δ 3.71-3.69 (m, 2 H), 3.66-3.61 (m, 10 H), 3.59-3.57 (m, 2 H), 3.54-3.52 (m, 2 H), 3.35 (s, 3 H), 2.84 (s, 1 H).

13-chloro-2,5,8,11-tetraoxatridecane (10)²: to solution of **9** (1.50 g, 7.20 mmol) in toluene (20 mL) were added SOCl₂ (0.63 mL, 8.64 mmol, 1.2 eq) and Et₃N (1.20 mL, 8.64 mmol, 1.2 eq). The resulting mixture was refluxed overnight. The mixture was filtered and the solid was washed with EtOAc. The filtrate was concentrated in vacuo. The crude product **10** (1.57 g, 96% yield) was put into next step directly without further purification. ¹H NMR (500 MHz, CDCl₃)³ δ 3.75-3.73 (m, 2 H), 3.65-3.60 (m, 12 H), 3.55-3.53 (m, 2 H), 3.37 (s, 3 H).

N,N-dimethyl-2,5,8,11-tetraoxatridecan-13-amine (11)⁴: to solution of **10** (1.00 g, 4.41 mmol) in CH₃CN (20 mL) were added K₂CO₃ (0.91 g, 6.62 mmol, 1.5 eq), KI (1.10 g, 6.62 mmol 1.5 eq), Me₂NH (38% in water, 2.35 mL, 17.64 mmol, 4.0 eq). The resulting mixture was refluxed over 18 h. The mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/CH₃OH = 4 : 1) to afford **7** (0.91 g, 88% yield) as yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 3.63-3.59 (m, 10 H), 3.57-3.51 (m, 4 H), 3.36 (s, 3 H), 3.48 (t, *J* = 7.5 Hz, 2 H), 2.33 (s, 6 H).



N-(4-(octyloxy)phenyl)acetamide (3): to a solution of **2** (5.00 g, 33.08 mmol) in acetone (50 mL) were added the 1-bromooctane (7.43 mL, 43.00 mmol, 1.3 eq) and K_2CO_3 (5.94 g, 43.00 mmol, 1.3 eq), and the resulting mixture was refluxed over 36 h. Then the reaction mixture was poured into water, and the resulting solid was filtered, dried and washed with petroleum ether. The obtained colorless solid **3** was put into next step directly without further purification. **4-(octyloxy)aniline (4):** To a solution of crude product **3** from last step in MeOH (15 mL) was added HCl (37%, 10 mL), and the resulting solution was refluxed over 8 h. The mixture was cooled to room temperature, and the obtained crystal was filtered, washed with water and dried to afford **4**·HCl (7.68 g, 90% yield over two steps) as colorless solid. ^1H NMR spectra coincided with those reported in the literature.⁵

4-((4-(octyloxy)phenyl)diazenyl)phenol (5): To a solution of **4**·HCl (4.00 g, 15.52 mmol) in mixed solvents of acetone and water (120 mL, 3 : 1) were added HCl (37%, 1.29 mL, 15.52 mmol) and a solution of NaNO_2 (1.07 g, 15.52 mmol, 1.0 eq) in water (5 mL) at around 0 °C. The mixture was added to a mixture solution of phenol (1.75 g, 18.62 mmol, 1.2 eq) and NaOH (1.74 g, 43.46 mmol, 2.8 eq) in water (30 mL). The mixture was stirred in the ice-water bath, which was allowed to warm to room temperature overnight. The mixture was neutralized with 3 M HCl (aq), and the obtained brown solid was filtered, washed with water and dried to afford **5** (1.56 g). The aqueous filtrate was extracted with CH_2Cl_2 , and the combined organic layers were dried over Na_2SO_4 , concentrated in vacuo. The residue was purified by column chromatography on silica gel

(petroleum ether/EtOAc = 6 : 1) to afford **5** (1.63 g). **5** was obtained as brown solid in 63% yield in total. ¹H NMR (400 MHz, CDCl₃)⁵ δ 7.86 (d, *J* = 9.2 Hz, 2 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 6.98 (d, *J* = 9.2 Hz, 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 4.03 (t, *J* = 6.4 Hz, 2 H), 1.85-1.78 (m, 2 H), 1.51-1.44 (m, 2 H), 0.84-0.88 (m, 8 H), 0.89 (t, *J* = 6.8 Hz, 3 H).

1-(4-(4-bromobutoxy)phenyl)-2-(4-(octyloxy)phenyl)diazene (6): to a solution of **5** (800 mg, 2.45 mmol) in acetone (20 ml) were added 1,4-dibromobutane (0.35 mL, 2.94 mmol, 1.2 eq) and K₂CO₃ (1.02 g, 7.35 mmol, 3 eq). The mixture was refluxed over 24 h. After cooling to room temperature, the solid of mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc/DCM = 10 : 1 : 1) to afford **6** (881 mg, 78% yield) as yellow solid. ¹H NMR (400 MHz, CDCl₃)⁶ δ 7.87 (d, *J* = 8.8 Hz, 4 H), 7.00-6.97 (m, 4 H), 4.08 (t, *J* = 6.0 Hz, 2 H), 4.03 (t, *J* = 6.4 Hz, 2 H), 3.51 (t, *J* = 6.4 Hz, 2 H), 2.13-2.07 (m, 2 H), 2.02-1.96 (m, 2 H), 1.85-1.78 (m, 2 H), 1.51-1.44 (m, 2 H), 1.38-1.26 (m, 8 H), 0.91-0.88 (m, 3 H).

***N,N*-dimethyl-*N*-(4-(4-((4-(octyloxy)phenyl)diazenyl)phenoxy)butyl)-2,5,8,11-**

tetraoxatridecan-13-aminium bromide (1): to a solution of **6** (500 mg, 1.08 mmol) in CH₃CN (15 mL) was added **11** (204 mg, 0.87 mmol, 0.8 eq). After being stirred under reflux overnight, the mixture was concentrated in vacuo. The residue was added EtOAc, and the solid product was filtered. The obtained solid was washed with EtOAc and dried. **1** (670 mg, 89% yield) was obtained as light orange solid. ¹H NMR (500 MHz, CDCl₃): δ 7.84-7.82 (m, 4 H), 6.98-6.95 (m, 4 H), 4.09 (t, *J* = 6.0 Hz, 2 H), 4.01-3.95 (m, 4 H), 3.88-3.87 (m, 2 H), 3.76-3.72 (m, 2 H), 3.64-3.62 (m, 2 H), 3.57-3.56 (m, 8 H), 3.50-3.49 (m, 2 H), 3.38 (s, 6 H), 3.33 (s, 3 H), 2.03-1.97 (m, 2 H), 1.92-1.89 (m, 2 H), 1.81-1.76 (m, 2 H), 1.48-1.42 (m, 2 H), 1.35-1.23 (m, 8 H), 0.87 (t, *J* = 6.5 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 161.2, 160.4, 147.1, 146.7, 124.3 (C_o*2 + C_p*2), 114.62 (C_q*2), 114.60 (C_n*2), 71.8, 70.4, 70.33, 70.30, 70.28, 70.1, 68.3, 67.0, 65.4, 64.9, 63.2, 58.9, 51.9 (-CH₃*2), 31.7, 29.3, 29.14, 29.12, 25.93, 25.86, 22.6, 19.8, 14.0; HRMS (ESI) calcd. for C₃₅H₅₈N₃O₆ [M - Br]⁺ 616.4320, found 616.4318.

***N,N,N*-trimethyl-4-(4-((4-(octyloxy)phenyl)diazenyl)phenoxy)butan-1-aminium bromide (7)**: **7**, yellow solid, was prepared from **6** in 95% yield following a procedure similar to that for **1**. ¹H NMR spectra coincided with those reported in the literature.⁶

3. UV-Vis absorption spectra

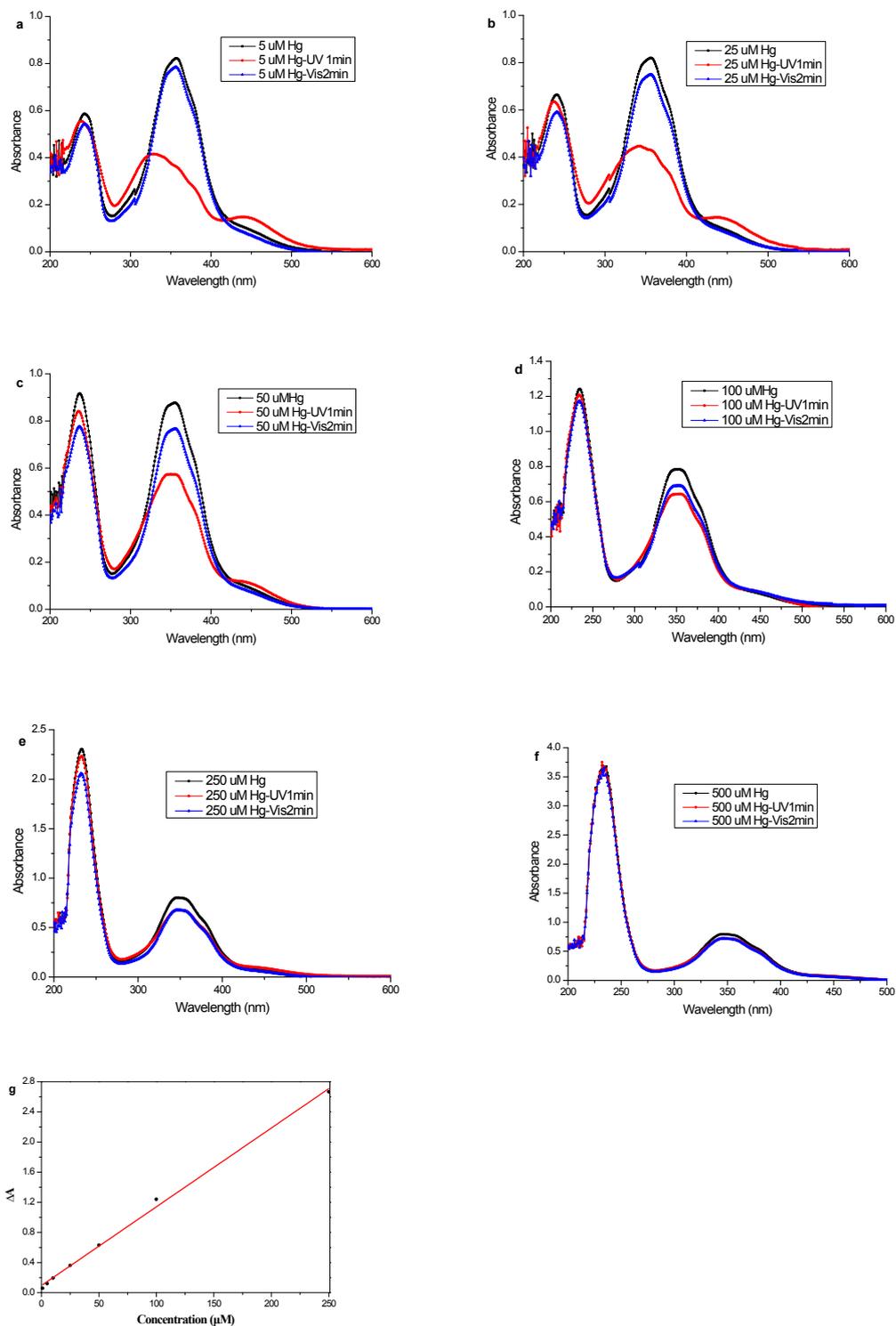


Figure S1. **a-f)** UV-Vis absorption spectral changes of **1** (50 μM) upon addition of different concentrations of Hg^{2+} in buffered aqueous solutions after UV and visible light irradiations, respectively; **g)** the linear relationship between absorption intensity ($\Delta A = A_{1+\text{Hg}} - A_1$) at band 240 nm of **1** and concentration of Hg^{2+} ranging from 1 to 250 μM , $R^2 = 0.9966$.

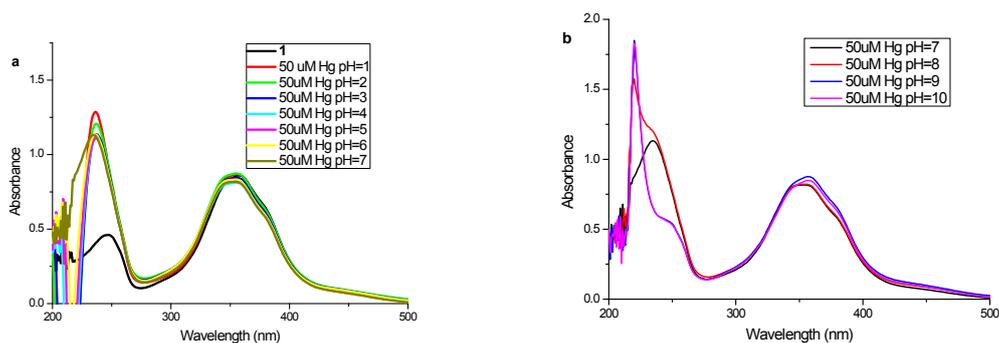


Figure S2. UV-Vis absorption spectral changes of **1**-Hg²⁺ (50 μM - 50 μM) under different pH values in buffered aqueous solutions.

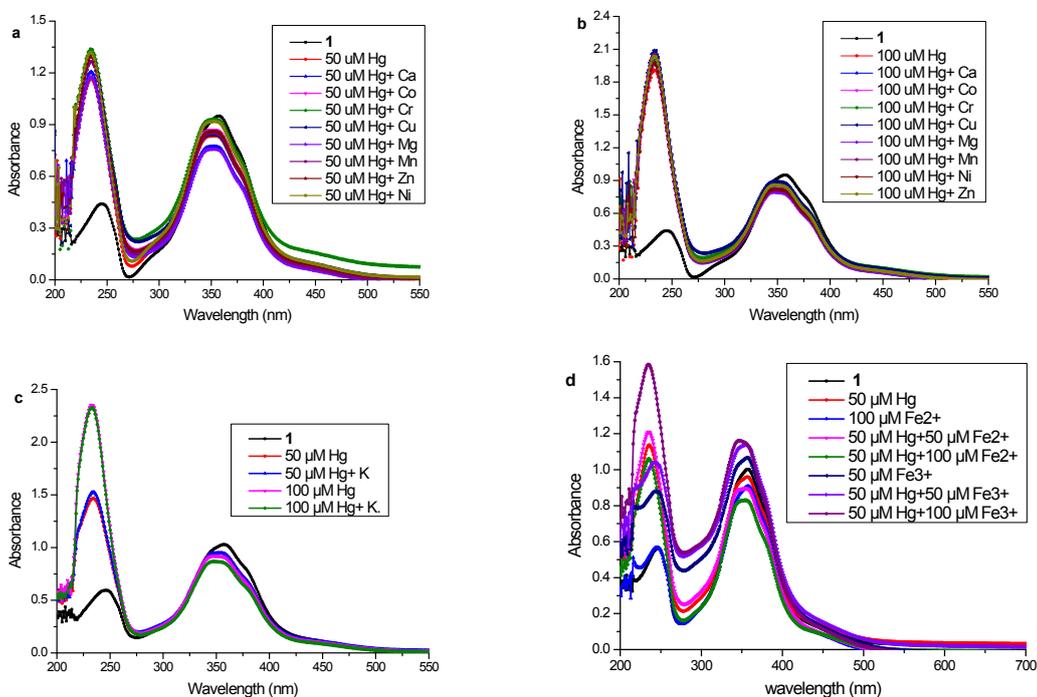


Figure S3. UV-Vis absorption spectral changes of **1**-Hg²⁺ upon addition of different metal ions in aqueous solutions: **a**) 50 μM **1** + 50 μM Hg²⁺ + 50 μM metal ions; **b**) 50 μM **1** + 100 μM Hg²⁺ + 100 μM metal ions; **c**) 50 μM **1** + 50 or 100 μM Hg²⁺ + 50 or 100 μM K⁺. **d**) UV-Vis absorption spectral changes of **1** upon addition of iron ions and subsequent addition of Hg²⁺ in aqueous solutions with concentration of 50 μM **1** + 50 or 100 μM iron ions + 50 μM Hg²⁺.

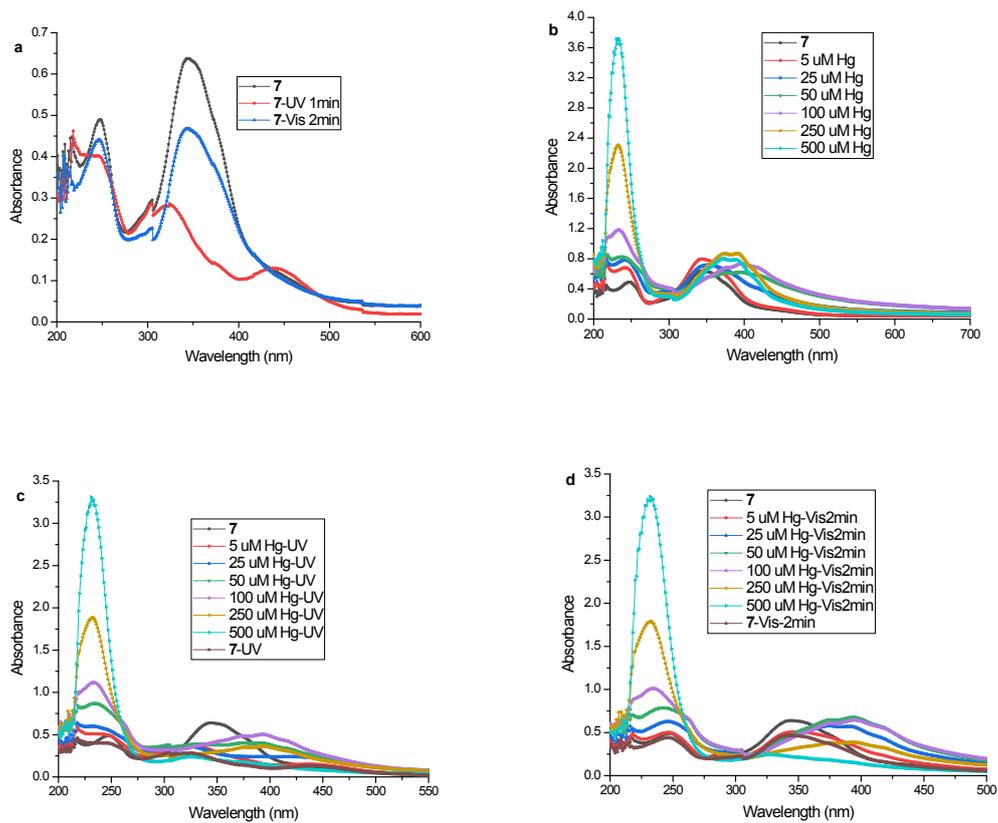


Figure S4. UV-Vis absorption spectral changes of **7** (50 μM) in buffered aqueous solutions **a**) after UV and visible light irradiation respectively; **b**) upon addition of Hg²⁺; **c**) upon addition of Hg²⁺ after UV irradiation over 1 min; **d**) upon addition of Hg²⁺ after Vis irradiation over 2 min.

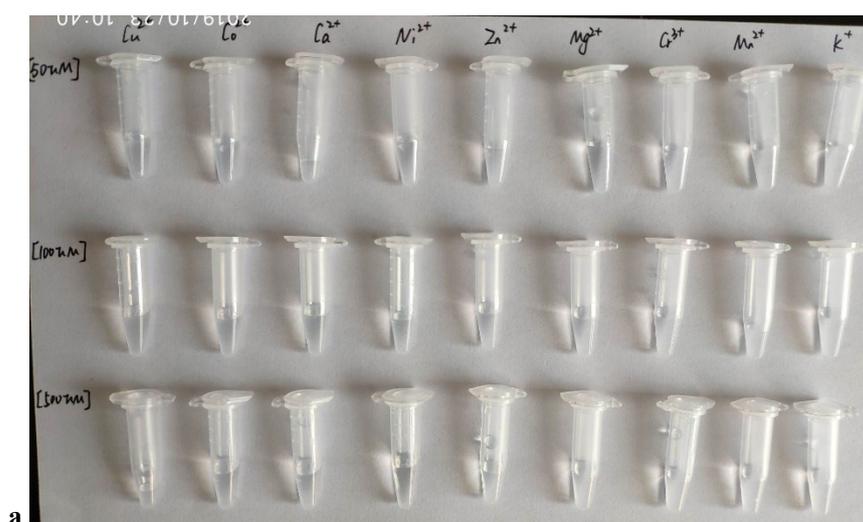




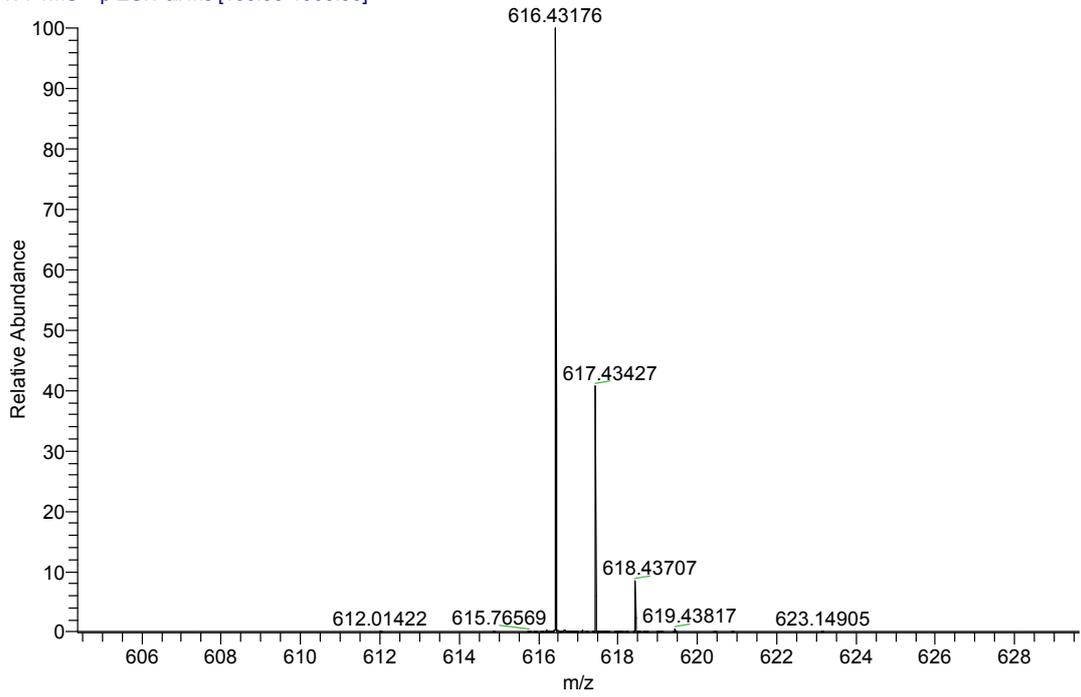
Figure S5. Colors of **a**) different concentrations of metal ions; **b**) **1** (marked as **L** in the pictures), **1** + metal ions (100 μM), **1** + metal ions (100 μM) + Hg^{2+} (50 μM); **c**) **1** (marked as **L** in the pictures), **1** + metal ions (500 μM), **1** + metal ions (500 μM) + Hg^{2+} (50 μM).

4. References

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2,5,8,11-tetraoxatridecan-13-ol (9)

